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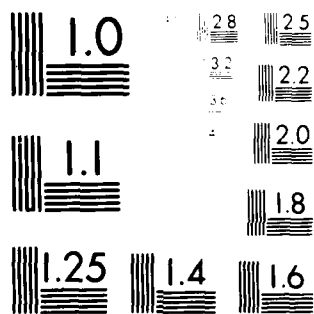UNCLASSIFIED   TR-26   NL

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Technical Report #26

State Selected Velocity Measurements: NO/Ru(001) Thermal Desorption

David S. King and Richard R. Cavanagh

Molecular Spectroscopy Division
National Bureau of Standards
Washington, DC 20234

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The tangential velocity distribution of ground-state NO (J" = 9 1/2, E_{rot}=165 cm^{-1})thermally desorbed from Ru(001) under ultrahigh vacuum conditions was measured by laser excited fluorescence Doppler spectroscopy. The measured Doppler profile was Gaussian in nature, characterized by a temperature $T_{//}$=235 $\pm$ 45 K significantly lower than the surface temperature at the desorption peak of 455 K.

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NO/Ru(001) Thermal Desorption

by

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Molecular Spectroscopy Division

Washington, D.C. 20234   USA

ABSTRACT

The tangential velocity distribution of ground state
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A

Quantum-state specific studies of the interactions of molecules with clean, well-characterized metal surfaces are quite sparse. Molecular beam scattering has been utilized to examine angular and velocity distributions of translationally-inelastic scattered particles.[1] Very recently, laser excited fluorescence (LEF) techniques have been applied to the measurement of the change in rotational state[2] and rotational alignment[3] for molecular beam scattering of NO from Ag(111), the rotational distribution of NO thermally desorbed from Ru(001) [4], and Doppler profiles of sputtered atoms[5]. To date there have been no rotational state specific measurements of translational energy for either inelastic beam/surface scattering or thermal desorption.

We report here the first measurement of a rotational-state specific velocity distribution for thermally desorbed molecules from a single crystal metal under ultra-high vacuum (UHV) conditions. The experiment is based on the measurement of a molecular Doppler profile using LEF techniques[6]. The absorption frequency ν for a molecule moving with a velocity $\vec{v}$ relative to the propagation direction of the exciting laser $\vec{n}$ (unit) be shifted in frequency: $\nu = \nu_0(1+\vec{v}\cdot\vec{n}/c)$, where c is the speed of light. Under the conditions of thermal equilibrium, a Maxwell-Boltzmann distribution of velocities and their corresponding Doppler shifts give rise to the Gaussian line-shape function:

$$S_d(\nu,\nu_0) = S_0 \exp[-(\ln 2)\left(\frac{\nu-\nu_0}{(\Delta\nu)_d}\right)^2] \quad . \tag{1}$$

Given such an equilibrium distribution, the Doppler width (FWHM) $2(\Delta\nu)_d$ is only dependent on the translation temperature.

The sample chamber used in this work was a stainless steel UHV apparatus equipped with an ion pump, titanium sublimators, effusive molecular beam doser, and quadrupole mass spectrometer[4]. All experimental results reported here were obtained following saturation NO coverage of the freshly cleaned and cooled(273 K) Ru crystal and using a 12 K sec^{-1} heating rate.

The molecularly desorbed NO was probed by exciting the origin of the lowest lying $\tilde{A}$ ^{2} Σ^+ -- $\tilde{X}$ ^{2} $\Pi_{1/2}$ electronic transition[7]. The ultraviolet probe laser beam was collimated with a beam area of 0.1 cm^2. In the UHV chamber the probe beam passed parallel to the 0.7 x 0.7 cm crystal.face at a distance of about 0.5 cm. After traversing the UHV chamber, the laser passed through a reference cell and into an absolute energy meter. The spectral bandwidth of the visible dye laser fundamental was measured to be $\leq$ 0.015 cm^{-1}. We estimate the bandwidth of the frequency doubled probe to be ~ 0.02 cm^{-1}. The probe laser energy of 10 μJoule in a 10 nsec duration pulse was well below the NO saturation requirement of 1 mJoule/cm^2 . The accuracy of the Doppler measurements was determined by observing single NO ro-vibronic line profiles in the reference cell. The room temperature Doppler width for NO is $2(\Delta\nu)_d \approx 0.086$ cm^{-1}; the line profiles obtained for a 46 x 10^{-6} mixture of NO in nitrogen at an NO density of 10^{11} cm^{-3} was Gaussian between the e^{-2} points with a measured FWHM of 0.088 $\pm$ 0.004 cm^{-1}.

In these thermal desorption experiments, evolution of NO into the gas phase only occurs during a four second interval as the crystal

temperature linearly increases from 435 - 475 K. Thus, only a
single frequency component of the full Doppler profile for any
individual ro-vibronic transition could be measured during an individual
desorption flash. As the Ru crystal was being cycled through the
annealing/dosing procedure the laser frequency was tuned to measure
a new velocity component within the same ro-vibronic band. The
reference cell LEF was always recorded simultaneously for normalization
purposes and to provide an independent verification of v_0. The
recovered ratioed signal is:

$$I_{J''}(v) = \frac{{}^{TPD}N_{J''}(v)}{{}^{ref}N_{J''}(v)} \times C^{-1} \quad , \tag{2}$$

where ${}^{TPD}N_{J''}(v)$ represents the number density of
thermally desorbed species in rotational
state J" with the appropriate parallel velocity component to absorb
at the Doppler shifted frequency v, and C is the relative detection
efficiency of the two optical systems. ${}^{ref}N_{J''}(v)$ is a Maxwell-Boltzmann
distribution with a temperature of 293 ± 2 K. ${}^{TPD}N_{J''}(v)$, which has
never been previously characterized, is obtained from eqns. (1) and (2).
In the figure, the thermal desorption tangential Doppler line shape
for NO molecules with 165 cm^{-1} of rotational energy (J" = 9 1/2) is
plotted. The data represent the average and standard deviations of
5-8 individual flash desorption measurements with peak NO (J"=9 1/2)
densities on the order of 10^6 cm^{-3}. The error bars reflect the
reproducibility of the thermal desorption experiments, random shot
noise and laser scatter, and slight frequence jitter of the probe laser

frequency. The solid curve represents the Gaussian line profile determined to give the best least squares fit to the experimental data. The data fall symmetrically about ν_0 and correspond to a tangential translational temperature of $T_{//}(E_{rot}=165 \text{ cm}^{-1}) = 235 \pm 45 \text{ K}$ (at the 95% confidence level).

The important result of this work is that the tangential Doppler profile of ground state NO molecules in the J"=9 1/2 rotational level thermally desorbed from Ru(001) is characterized by a translational temperature significantly lower than the surface temperature.of 455 K. One aspect of thermal desorption predicted by statistical theories, such as transition state theory, is full equilibration of the tangential velocity with the surface[8]. This is clearly not obtained in the NO/Ru(001) system. Similar effects have been observed in the gas phase where the partitioning of excess reaction energy over internal degrees of freedom and relative translational energy need not reflect the transition state but rather may arise from exit channel effects[9]. Whether the deviation from statistical behavior observed for NO/Ru(001) is an exit channel effect or represents a dynamical bias[10] in the thermal desorption process is, at this early point, unknown. We are currently measuring the dependence of $T_{//}$ on rotational state and the angular distribution of desorbing species. The results of these studies will be presented in a full manuscript including further experimental detail.

FIGURE CAPTION: Laser Doppler profile of NO ($J''=9\ 1/2$, $E_{rot}=165\ cm^{-1}$) thermally desorbed from Ru(001) as measured parallel to the crystal face. The crystal temperature at the thermal desorption maximum was 455 K. The laser bandwidth was 0.02 cm^{-1} and the zero Doppler shift frequency was 44,252 cm^{-1}. Least squares fitting to a Gaussian line profile gave a tangential velocity distribution characterized by the temperature $T_{//}(J''=9\ 1/2)=235 \pm 45$ K.
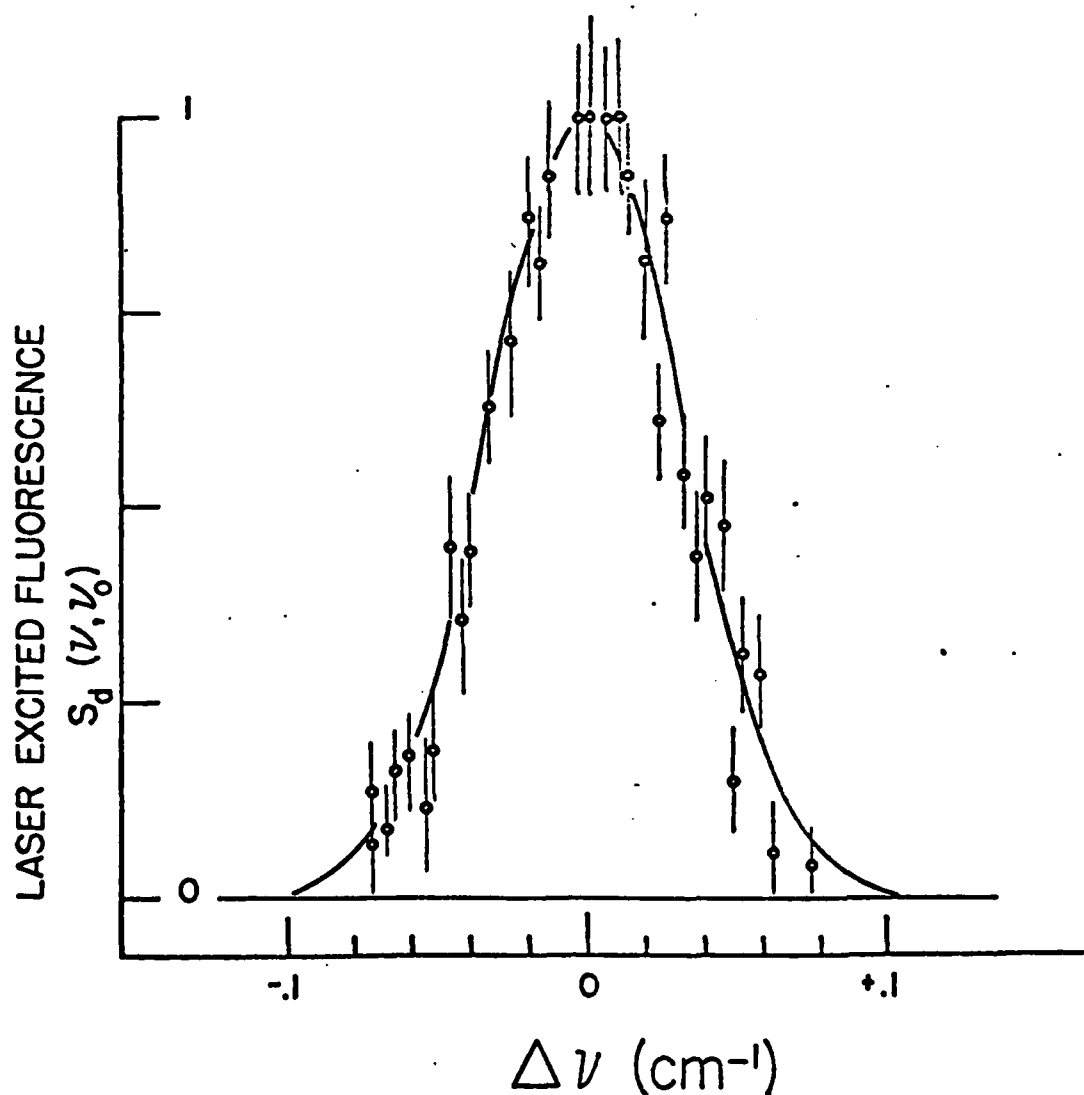
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